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COMPLETE SPECIFICATION

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:—ROGER CHARLE, GREGOIRE KALOPISSIS and JEAN GASCON of 61 Avenue Gavignot Soisy-Sous-Montmorency (Seine et Oise), France, 64, rue Vauvenargues Paris, France and 11 rue Lourmel, Paris, France respectively, a French citizen, a Greek subject and a French citizen respectively.

A method of Dyeing Hair and Compositions for use in the method

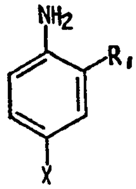
We, L'OREAL, a French Body Corporate, of 14 Rue Royale, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of dyeing hair using *para*-diaminobenzene derivatives and couplers, and to compositions for use in that method.

It is well known in the art of dyeing hair to use primary *para*-diamines in conjunction with couplers to obtain various shades of colour. However, the prior procedures were not satisfactory, because the colours obtained were not fast to light. Moreover, it was difficult to produce a predetermined shade by reason of the fact that the final shade results from the superimposition of two dyes, namely the amine used and a second dye obtained by interaction of the amine with the coupler.

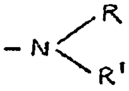
The present invention relates to a new method of dyeing hair which has not the aforesaid disadvantages because the dyes formed have exceptional fastness to light, at least in regard to the times, of the order of one year, which are relevant to hair dyeing. On the other hand, the amine employed does not in itself possess any satisfactory colouring power, so that the shade obtained results from the interaction of the coupler with the amine.

The method of the present invention comprises applying to the hair: (a) an amine of the formula:—



(I)

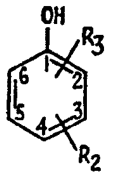
in which R_1 represents a hydrogen atom, or a methyl, ethyl or propyl radical and X represents the group



in which R is a methyl, ethyl or propyl radical and R′ is

$$—CH_2CONH_2,\ —CH_2COOH,\ —CH_2CH_2NHSO_2CH_3 \text{ or } —CH_2CON(C_2H_5)_2,$$

or an *N*-piperidyl or N-morpholyl radical; (b) one or more couplers of one of the following formulae:



(II)

in which R_2 represents hydrogen and R_3 represents a methoxy radical in the 4-position, or R_2 represents hydrogen or a methyl radical in the 6-position and R_3 represents $—CH_3$,

$—NHCOCH_3$, $—NHCH_2CONH_2$,

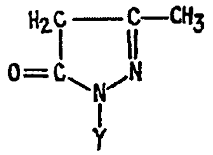
$—NHCH_2CON(C_2H_5)_2$ or

$—NHCOCH_2N(C_2H_5)_2$

in the 3-position;

$$R_4—CO—CH_2—CO—R_5 \quad (III)$$

in which R_4 represents methyl and R_5 represents methyl or ethoxy, or R_4 represents phenyl and R_5 represents *p*-carboxyphenylamino or *m*-carboxyphenylamino; or



(IV)

in which Y represents an phenyl, *p*-sulphophenyl, *m*-sulphophenyl or a 2-chloro-5-sulphophenyl radical; and

(c) an oxidizing agent; allowing sufficient time to elapse after the application for the dyeing effect to be obtained, then removing any unwanted excess of components (a), (b) or (c) from the hair.

The amine and coupler can be used, where appropriate, in the form of their salts.

The method can conveniently be carried out by applying the said amine and the said coupler in the form of aqueous solutions in consecutive order to the hair, and the oxidizing agent can be conveniently in either the solution of amine or coupler.

The solutions can contain other dyestuffs which may be employed under the same conditions as direct dyes, for example azo dyes. They can also contain wetting agents, dispersing agents, penetration agents and other ingredients generally employed in hair dyeing.

A great variety of shades of colour can be obtained using the method of the invention. When utilized with one or several amines, the couplers of formula (II) provide shades of blue, the couplers of formula (III) provide shades of yellow and the couplers of formula (IV) provide shades of red.

It is therefore possible to obtain a very considerable range of colours by associating a given coupler with a given amine, but—and this is one of the most important features of the invention—it is possible when using a given amine and a mixture of two couplers belonging to two of the formulae (II), (III) or (IV) to obtain, by varying the proportions of couplers, all shades between the colours obtained with each of the two couplers used by itself. Similarly, by using a given coupler, a variety of colours can be obtained, although to a smaller degree, by using various amines of the formula (I).

It will be seen that by using a limited number of amines and couplers it is possible to cover the whole range of shades appropriate for hair dyes.

The dyes obtained using the method of invention have proved to have exceptional resistance to light as compared with dyes hitherto used for hair dyeing. Moreover, a study of the toxicity of the dyes provided by the present invention has shown, contrary to what might have been expected, that they are probably less toxic, and in any case not more toxic, than the dyes based upon *p*-phenylenediamine which are at present in use for hair dyeing, which themselves produce appreciable allergy reactions only in extremely rare cases.

Finally, the amines of formula (I) have the advantage that they do not impart any colour to the hair when applied in the absence of couplers. By virtue of this property, the colours obtained using the present invention result essentially from the combination of the amine and of the coupler and not from the superimposition of two distinct colours, as is the case in the majority of dyeing solutions hitherto employed. This property is most valuable in practice, because it has been observed that the shades obtained in the earlier processes vary from one person to another and even from one place to another on the same hair by reason of a selectivity in the "taking" of the amines and the couplers on the hair, which disadvantage is avoided with the invention since the colour obtained results only from the amine-coupler association.

The invention is illustrated by the following Examples.

EXAMPLE 1

There is prepared a solution having the following composition:

4 - amino - 3 - methyl - *N* - ethyl - *N* - [β - (methylsulphamido)-ethyl]aniline sulphate	2.9 g.
2,5-dimethylphenol	1.22 g.
sodium hydroxide	0.2 g.
ethyl alcohol	10 cc.
ammonia solution (22°Bé)	6 cc.
water q.s. for	50 cc.

The pH of this solution is 10.5.

This solution, which can be kept without deteriorating, is mixed at the time of use with an equal volume of hydrogen peroxide (20 vol.), and when applied to white hair dyes it blue. The method of dyeing in this and in the following examples consisted of applying the dyeing solution to the hair at ambient temperature, leaving the hair for 20 minutes and then successively rinsing, shampooing, rinsing again and drying.

EXAMPLE 2

There is prepared a solution having the following composition:

4-amino-3-methyl-*N*-ethyl-*N*-carbamylmethylaniline sulphate	1.28 g.
3-*N*-acetamino-6-methyl-phenol ammonia solution (22°Bé)	6 cc.
water q.s. for	50 cc.

The pH of this solution is 10.6. When mixed with an equal volume of hydrogen peroxide (20 vol.) and applied to white hair it gives a moderate blue colour.

EXAMPLE 3

There is prepared a solution having the following composition:

4-amino-*N*-ethyl-*N*-carbamylmethylaniline	0.97 g.
4-methoxyphenol	1.25 g.
ammonia solution (22° Bé)	6 cc.
water q.s. for	50 cc.

The pH of this solution is 10.6. When mixed with an equal volume of hydrogen peroxide (20 vol.) and applied to grey hair, it gives a greenish-greyish blue colour.

EXAMPLE 4

There is prepared a first solution A having the following composition:

N-(4-aminophenyl)morpholine sulphate	2.59 g.
3-acetaminophenol	3 g.
ammonia solution (22° Bé)	6 cc.
water q.s. for	50 cc.

This solution has a pH of 10.6.

There is also prepared a solution B having the following composition:

N-(4-aminophenyl)morpholine sulphate	2.59 g.
3-*N*-(carbamylmethylamino)phenol	2.32 g.
ammonia solution (22° Bé)	6 cc.
water q.s. for	50 cc.

This solution has a pH of 10.6.

There are added to 50 cc. of a mixture of these two solutions A and B, 50 cc. of hydrogen peroxide (20 vol.). Depending upon the ratio by volume of the two solutions A and B which have been mixed, there are obtained by dyeing white hair colours which range from purplish blue to light greyish brown.

EXAMPLE 5

There are prepared a solution C, identical to that described in example 3, and a solution D having the following composition:

4-amino-*N*-ethyl-*N*-carbamylmethylaniline	0.97 g.
1-phenyl-3-methyl-5-pyrazolone	0.88 g.
ammonia solution (22° Bé)	6 cc.
water q.s. for	50 cc.

This solution D has a pH of 10.6.

To 50 cc. of a mixture of these two solutions C and D are added 50 cc. of hydrogen peroxide (20 vol.)

Depending upon the proportions of the mixture of C and D, there are obtained upon dyeing grey hair colours ranging from purplish grey to blackish blue. Thus, with 40 volumes of C and 60 volumes of D a dark violet-grey is obtained; with 60 volumes of C and 40 volumes of D a dark bluish-grey is obtained; and with 80 volumes of C and 20 volumes of D a blackish-blue is obtained.

EXAMPLE 6

There is prepared a solution having the following composition:

4-amino-3-methyl-*N*-ethyl-*N*-[β-(methylsulphamido)-ethyl]aniline sulphate	2.9 g.
4-benzoylacetaminobenzoic acid	11.3 g.
ammonia solution (22° Bé)	25 cc.
water q.s. for	50 cc.

This solution, which has a pH of 10, can be kept well without decomposition. It is mixed with an equal volume of hydrogen peroxide (20 vol.) and applied immediately to white hair, giving a deep orange-yellow colour.

EXAMPLE 7

There is prepared a solution having the following composition:

N-(4aminophenyl)piperidine sulphate	2.39 g.
1-phenyl-3-methyl-5-pyrazolone	1.75 g.
ammonia solution (22° Bé)	8 cc.
water q.s. for	50 cc.

This solution, which has a pH of 10.7, can be kept well without decomposition. An equal volume of hydrogen peroxide (20 vol.) is added to the solution, and the mixture is applied immediately to white hair giving a dark purplish-red colour.

EXAMPLE 8

There is prepared a solution having the following composition:

N-methyl-*N*-(4′-aminophenyl)-α-aminoacetic acid	1.8 g.
3-methyl 1-(*p*-sulphophenyl)-pyrazol-5-one	2.55 g.
ammonia solution (22° Bé)	8 cc.
water q.s. for	50 cc.

This solution, which has a pH of 10.5, can be kept well without decomposition. By adding thereto an equal volume of hydrogen peroxide (20 vol.) and applying it to white hair, a pale reddish-purple colour is obtained.

EXAMPLE 9

There are prepared three solutions E, F and G, each containing:

4-amino-3-methyl-*N*-ethyl-*N*-[β-(methylsulphamido)ethyl]-aniline sulphate	2.9 g.

and respectively:

for E:	3-acetaminophenol	1.5 g.
	ammonia solution (22° Bé)	6 cc.
for F:	4-benzoylacetaminobenzoic acid	11.3 g.
	ammonia solution (22° Bé)	25 cc.
for G:	1-phenyl-3-methyl-5-pyrazolone	1.75 g.
	ammonia solution (22° Bé)	8 cc.

Each of these solutions is thereafter diluted with water to bring its volume to 50 cc. Two of these solutions are mixed in any proportions and there is added at the time of use a volume of hydrogen peroxide (20 vol.) equal to the volume of this mixture. Depending upon the proportions of the two solutions employed, the following results are obtained on white hair:—

E+F: all shades ranging from dark greenish-blue to deep orange-yellow;

F+G: all shades ranging from deep orange-yellow to dark purple-red;

G+E: all shades ranging from purple-red to dark greenish-blue.

Example 10

There are prepared a solution H, identical to that described in Example 2, and a solution J containing:

4,4′-dihydroxy-2-aminoazobenzene	0.50 g.
disodium phosphate (dihydrate)	0.9 g.
caustic soda q.s. for pH 10	
water q.s. for	50 cc.

To 50 cc. of a mixture of solutions H and J is added an equal volume of hydrogen peroxide (20 vol.). Depending upon the ratios of the volumes of solutions H and J, there are obtained on application of the mixture to white hair colours ranging from greenish-grey to bright orange-yellow.

Example 11

There is prepared a solution K, having the following composition:

4-amino-*N*-ethyl-*N*-carbamylaniline	1.93 g.
solution of ammonia (22° Bé)	6 cc.
water q.s. for	100 cc.

The pH of this solution K is 11. This solution is applied to grey hair at ambient temperature and after 20 minutes the hair is then rinsed with water.

There was also prepared a solution L containing:

3-acetaminophenol	2.25 g.
ammonia solution (22° Bé)	6 cc.
water q.s. for	100 cc.

The pH of this solution L is 10.6. Solution L is then applied for 20 minutes at ambient temperature to the hair previously treated with solution K, and after 20 minutes the hair is rinsed.

Finally, there is appled at ambient temperature to the hair, treated with solutons K and L, a solution M composed of:—

hydrogen peroxide (50 vol.)	50 cc.
ammonia solution (22° Bé)	6 cc.
water q.s. for	100 cc.

20 minutes after the application of solution M, the hair is rinsed, washed and dried. There is thus obtained a moderate blue colour in the hair.

Example 12

There is prepared a solution N having the following composition:—

3-acetaminophenol	2.25 g.
ammonia solution (22° Bé)	6 cc.
hydrogen peroxide (20 vol.)	50 cc.
water q.s. for	100 cc.

The pH of this solution is 10.6. Solution N is applied to the grey hair previously treated by solution K, as described in Example 11, and the same colour is obtained as in Example 11.

Example 13

There is prepared a solution containing:

4-amino-*N*-ethyl-*N*-carbamylmethylaniline	1.93 g.
solution N of Example 12 q.s. for	100 cc.

Application to grey hair for 20 minutes gives a colour identical to that obtained in accordance with Examples 11 and 12.

Example 14

White hair is treated with a solution containing:

3-[α-(*N′*,*N′*-diethyl)aminoacetamino]-phenol	1.11 g.
Aqueous solution of ammonia at 22° B	6 cc.
Water q.s.p.	100 cc.

After 20 minutes, hair is rinsed and treated with another solution containing:

4-amino-3-methyl-*N*-ethyl-*N*-carbamylmethylaniline sulphate	1.28 g.
Aqueous solution of ammonia at 22°B	6 cc.
Hydrogen peroxide solution	6 g.
Water q.s.p.	100 cc.

The colouring obtained after 20 minutes is grey-greenish.

Example 15

The operation is effected as for Example 14, the first solution being replaced by the solution as follows:

6-methyl-3-[α(*N′*,*N′*-diethyl)-aminoacetamino]-phenol	1.18 g.
Solution of ammonia in water at 22° Bé	6 cc.
Water q.s.p.	100 cc.

The colouring obtained is grey-greenish.

Example 16

A solution is prepared as follows:

4-amino-[N-ethyl-*N*-(*N′*,*N′*-diethyl)-carbamylmethyl]aniline chlorhydrate	1.45 g.
6-methyl-3-(N-carbamylmethyl)amino-phenol	2.22 g.
Aqueous solution of ammonia at 22° Bé	6 cc.
Water q.s.p.	50 cc.

The pH of said solution is 10.5

Said solution utilized in the same conditions as Example 1 with H_2O_2 produces a dark-blue colouring.

Example 17

A solution is prepared as follows:

4-amino-3-methyl[*N*-ethyl-*N*-(*N′*,*N′*-diethyl)-carbamylmethyl]aniline chlorhydrate	1.50 g.
3-acetamino-phenol	3 g.
Aqueous solution of ammonia at 22° Bé	6 cc.
Water q.s.p.	50 cc.

The pH of said solution is 10.6

Said solution applied in the same conditions as for Example 1 with hydrogen peroxide produces a light blue-greenish hue.

EXAMPLE 18

A solution is prepared as follows:

4 - amino - (*N* - ethyl - *N* - carbamylmethyl) - aniline chlorhydrate	1.15 g.
3 - [(*N'*,*N'* - diethyl) - carbamylmethyl] - amino - phenol	2.22 g.
Aqueous solution of ammonia at 22° Bé	6 cc.
Water q.s.p.	100 cc.

The pH of said solution is 10.6

When said solution is applied in the same conditions as mentioned for Example 2 with hydrogen peroxide, a crimson-grey hue is obtained.

EXAMPLE 19

A solution is prepared as follows

4 - amino - (*N* - ethyl - *N* - carbamylmethyl) - aniline chlorhydrate	1.15 g.
6 - methyl - 3 - [(*N'*,*N'* - diethyl)-carbamylmethylamino]phenol	2.36 g.
Aqueous solution of ammonia at 22° Bé	6 cc.
Water q.s.p.	100 cc.

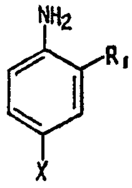
The pH of said solution is 10.6.

Said solution applied in the same conditions as mentioned in Example 1 with hydrogen peroxide, a dark crimson-grey hue is obtained.

As shown in the above Examples, the method of the present invention is not limited to the application to the hair of a solution containing together the amine, the coupler or couplers and hydrogen peroxide, but includes the successive application of different solutions each containing one or more of the ingredients.

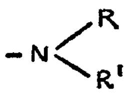
WHAT WE CLAIM IS:—

1. A method of dyeing hair, which comprises applying to the hair: (a) an amine of the formula:

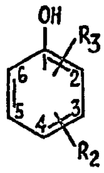


I

in which R_1 represents a hydrogen atom, or a methyl, ethyl or propyl radical and X represents the group



in which R is a methyl, ethyl or propyl radical and R′ is $—CH_2CONH_2$, $—CH_2COOH$, $—CH_2CH_2NHSO_2CH_3$ or $—CH_2CON(C_2H_5)_2$, or an *N*-piperidyl or *N*-morpholyl radical; (b) a coupler of one of the following formulae:

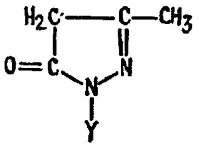


(II)

in which R_2 represents hydrogen and R_3 represents a methoxy radical in the 4-position, or R_2 represents hydrogen or a methyl radical in the 6-position and R_3 represents $—CH_3$, $—NHCOCH_3$, $—NHCH_2CONH_2$, $—NHCH_2CON(C_2H_5)_2$ or $—NHCOCH_2N(C_2H_5)_2$ in the 3-position;

(III) $R_4—CO—CH_2—CO—R_5$

in which R_4 represents methyl and R_5 represents methyl or ethoxy, or R_4 represents phenyl and R_5 represents *p*-carboxyphenylamino, or *m*-carboxyphenylamino; or



(IV)

in which Y represents a phenyl, *p*-sulphophenyl, *m*-sulphophenyl or a 2-chloro-5-sulphophenyl radical; and (c) an oxidizing agent: allowing sufficient time to elapse after the application for the dyeing effect to be obtained, then removing any unwanted excess of components (a), (b) or (c) from the hair.

2. A method according to claim 1, in which the said oxidizing agent is hydrogen peroxide.

3. A method according to claim 2, in which the hydrogen peroxide is applied to the hair in an aqueous solution of either the said amine or the said coupler.

4. A method according to claim 1, 2 or 3, in which the said amine, hydrogen peroxide and coupler are mixed together before being applied to the hair.

5. A method of dyeing hair using an amine and a coupler substantially as described herein.

6. A method of dyeing hair using an amine and a coupler substantially as described in any of the Examples.

7. A composition for use in dyeing the hair, comprising a mixture of an amine as defined in claim 1 and a coupler as defined in claim 1.

8. A composition for use in dyeing the hair, comprising a mixture of an amine as defined in claim 1 and an oxidizing agent.

9. A composition for use in dyeing the hair, comprising a mixture of a coupler as defined in claim 1 and an oxidizing agent.

10. A composition for use in dyeing the hair, comprising a mixture of an amine and a coupler, both as defined in claim 1, and an oxidizing agent.

11. A composition according to claim 8, 9 or 10, in which the said oxidizing agent is hydrogen peroxide.

12. A composition according to any of claims 7 to 11, containing a wetting agent, dispersing agent or penetration agent.

13. A composition according to any of claims 7 to 12, in the form of an aqueous solution whose pH is from 9 to 11.

14. A composition according to claim 13, in which the said pH is from 10.0 to 10.7.

15. A composition according to any of claims 7 to 14, which contains an azo dyestuff.

16. A composition for use in dyeing the hair comprising an amine and a coupler, substantially as described herein.

17. A composition for use in dyeing the hair comprising an amine and a coupler, substantially as described in any of the Examples.

18. A composition for use in dyeing the hair comprising an amine and a coupler, said amine being one of the following compounds:

4 - amino - 3 - methyl - *N* - ethyl - *N* - [β - (methylsulphamido)ethyl] aniline sulphate
4 - amino - 3 - methyl - *N* - ethyl - *N* - carbamylmethylaniline sulphate
4 - amino - *N* - ethyl - *N* - carbamylmethylaniline and its chlorhydrate
N - (4 - aminophenyl)morpholine sulphate
N - (4 - aminophenyl)piperidine sulphate
N - methyl - *N* - (4′ - aminophenyl) - α - aminoacetic acid
4 - amino[*N* - ethyl - *N* - (*N*′,*N*′ - diethyl) - carbamylmethyl] aniline chlorhydrate
4 - amino - 3 - methyl[*N* - ethyl,*N* - (*N*′*N*′- diethyl) - carbamylmethyl] aniline chlorhydrate.

19. A composition for use in dyeing hair comprising an amine and a coupler, said coupler being one of the following compounds:

6 - methyl - 3 - [(*N*′,*N*′ - diethyl)carbamylmethyl] - amino - phenol
2,5-dimethylphenol
3-*N*-acetamino-6-methyl-phenol
4-methoxyphenol
3-acetaminophenol
3-*N*-(carbamylmethylamino)phenol
1-phenyl-3-methyl-5-pyrazolone
4-benzoylacetaminobenzoic acid
3 - methyl - 1 - (*p* - sulphophenyl) - pyrazol - 5 -one
3-[α(*N*′*N*′-diethyl)amino] acetamino-phenol
6 - methyl - 3 - [α(*N*′*N*′ - diethyl) - amino - acetamino] - phenol
6 - methyl - 3 - (N - carbamylmethyl) - amino - phenol
3 - [(*N*′,*N*′ - diethyl) - carbamylmethylamino] - phenol.

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